

# Molecular adsorption of H<sub>2</sub> on small cationic nickel clusters<sup>†‡</sup>

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An H<sub>2</sub> molecule can bind molecularly on Ni<sub>4</sub><sup>+</sup> but it binds exclusively dissociatively on Ni<sub>5</sub><sup>+</sup> and Ni<sub>6</sub><sup>+</sup> and the adsorption behavior correlates with the relative reactivity of the metal clusters towards H<sub>2</sub>.

The adsorption of H<sub>2</sub> on metal clusters is of interest in several fields, including metallurgy, catalysis and hydrogen storage. Hydrogen interacting with small Ni clusters is of special interest, as Ni is widely used as a hydrogenation catalyst. In general, reactions of H<sub>2</sub> with extended Ni surfaces are well studied, both experimentally<sup>1</sup> and theoretically.<sup>2</sup> In practically all cases an H<sub>2</sub> molecule dissociates upon adsorption on a Ni surface and the H atoms bind in high coordination sites. The dissociation of H<sub>2</sub> on Ni is direct, *i.e.* it does not proceed *via* a molecular precursor state.<sup>1,3</sup> H<sub>2</sub> molecules can only bind molecularly on the step sites of a Ni(510) surface if this surface is fully saturated with H atoms.<sup>4</sup> Small Ni clusters do not necessarily exhibit the same behavior as extended surfaces. Consequently, the reaction of gas-phase Ni clusters with H<sub>2</sub> has been the subject of many studies.<sup>5–8</sup> However, detailed information on H binding sites on Ni clusters is scarce. In agreement with what is observed for extended Ni surfaces, it has recently been confirmed by IR spectroscopy that H<sub>2</sub> can be molecularly adsorbed on hydrogen saturated Ni clusters.<sup>9</sup> It is not clear whether H<sub>2</sub> binds molecularly to nickel clusters only once all sites for dissociative adsorption are blocked, or whether already the very first H<sub>2</sub> molecule can bind molecularly.

Here we report on a vibrational spectroscopy study, complemented with density functional theory (DFT) calculations, on the adsorption of a single H<sub>2</sub> molecule on Ni<sub>*n*</sub><sup>+</sup> clusters with *n* = 4–6. It will be shown that the first H<sub>2</sub> molecule can bind molecularly on Ni<sub>4</sub><sup>+</sup>, but that it binds exclusively dissociatively on Ni<sub>5</sub><sup>+</sup> and Ni<sub>6</sub><sup>+</sup>. Infrared multiple photon dissociation (IR-MPD) spectroscopy has been used to measure the vibrational spectra of Ni<sub>*n*</sub>H<sub>2</sub><sup>+</sup> complexes in the Ni–H stretch and deformation range as well as in the hydrogen–hydrogen stretch range. The setup and experimental

procedures have been described in detail elsewhere.<sup>10,11</sup> Briefly, metal clusters are generated in a laser ablation source. They pass through a reactor channel where reaction with H<sub>2</sub> occurs under thermalized conditions (at ~25 °C). The extent of complex formation is controlled by adjusting the opening time of the H<sub>2</sub> inlet valve on the reactor channel and the back pressure of H<sub>2</sub> behind that valve. A molecular beam is formed after expansion out of the reactor channel. This beam is shaped by a skimmer and an aperture before being overlapped with a counter-propagating beam of IR photons delivered by the free electron laser for infrared experiments (FELIX).<sup>12</sup> When the laser frequency is resonant with an IR-active vibration of a complex, several photons can be absorbed by the complex and it subsequently can undergo fragmentation. The vibrational spectra can be reconstructed by monitoring the changes in the cluster mass distribution as a function of photon frequency. Deuterium was used to probe the high frequency range because the D–D stretch vibration is located in a spectral range that is easier accessible with FELIX. To prevent congestion of the mass spectra, an isotopically enriched <sup>58</sup>Ni rod was used.

In Fig. 1A, three mass spectra, measured at different H<sub>2</sub> partial pressures in the reactor, are shown. A clear dependence of the reactivity on cluster size is observed. At low hydrogen content Ni<sub>5</sub><sup>+</sup> and Ni<sub>6</sub><sup>+</sup> already bind H<sub>2</sub> but no Ni<sub>4</sub>H<sub>2</sub><sup>+</sup> is found. The Ni<sub>4</sub>H<sub>2</sub><sup>+</sup> complex can only be formed by increasing the hydrogen content in the reactor further. At those pressures, Ni<sub>5</sub><sup>+</sup> and Ni<sub>6</sub><sup>+</sup> already bind multiple H<sub>2</sub> molecules. The differences in reactivity can be quantified by assuming that the addition of the first H<sub>2</sub> molecule is irreversible and rate determining in the process of adsorption of multiple H<sub>2</sub> molecules.<sup>7</sup> Since the molecular H<sub>2</sub> is present in excess, the depletion of the bare nickel clusters should then follow pseudo-first-order kinetics. Assuming that the hydrogen partial pressure in the reactor channel is proportional to the backpressure of H<sub>2</sub> in the pulsed valve, a semilogarithmic plot of the fraction of bare Ni clusters remaining at a certain H<sub>2</sub> concentration, *f*, versus the back pressure should give a straight line with a slope proportional to the rate constant. Such plots are shown in Fig. 1B. The good fit of the experimental data to the pseudo-first-order model indicates that the kinetic scheme outlined above is a reasonable approximation. Under the assumption that the reaction time is similar for all

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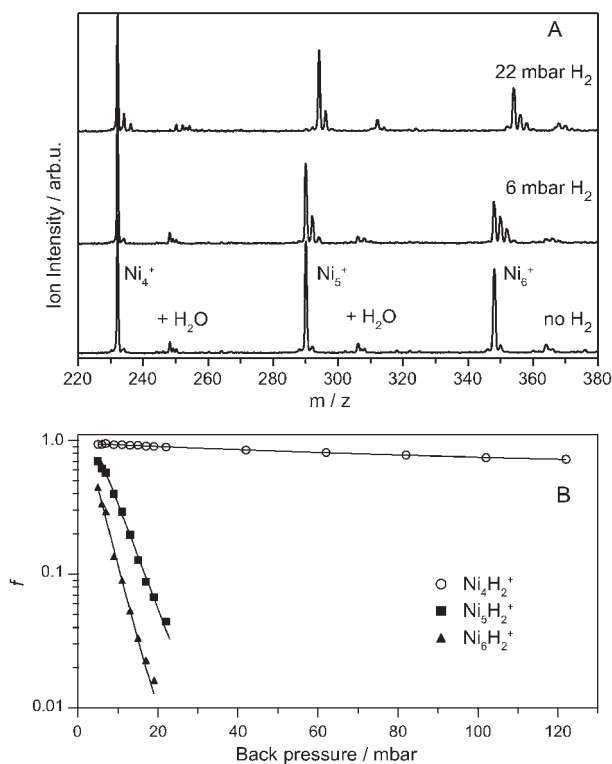
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<sup>‡</sup> This paper is dedicated to David M. Rayner on the occasion of his 60th birthday.

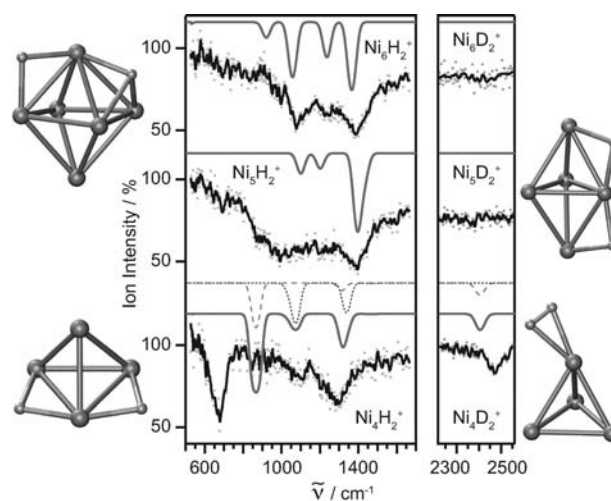


**Fig. 1** A. Mass spectra taken at various H<sub>2</sub> concentrations in the reactor, using backpressures ranging from no H<sub>2</sub> (bottom) to 22 mbar (top). Several peaks due to nickel water complexes are present in the spectrum. B. Semilogarithmic plot of the fraction of unreacted Ni clusters,  $f$ , versus the H<sub>2</sub> back pressure.

cluster sizes, the relative reactivity of Ni<sub>4</sub><sup>+</sup>, Ni<sub>5</sub><sup>+</sup>, and Ni<sub>6</sub><sup>+</sup> toward H<sub>2</sub> scales as 1 : 65 : 85. This differs significantly from the ratio of the rate constants for the formation of Ni<sub>5</sub>D<sub>2</sub><sup>+</sup> and Ni<sub>6</sub>D<sub>2</sub><sup>+</sup> measured under single collision conditions ( $0.15 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  and  $2.3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ , respectively).<sup>5</sup> These differences can be understood by a rapid stabilization of the complex *via* collisional thermalization in our reaction channel, which is missing under single collision conditions.

Consistent with the high reactivity of Ni<sub>5</sub><sup>+</sup> and Ni<sub>6</sub><sup>+</sup>, collision induced dissociation experiments have found no significant barriers for the formation of Ni<sub>5</sub>D<sub>2</sub><sup>+</sup> and Ni<sub>6</sub>D<sub>2</sub><sup>+</sup>. Ni<sub>4</sub>D<sub>2</sub><sup>+</sup> is not stable after formation under single collision conditions.<sup>5</sup> Barriers to the formation of M<sub>n</sub>D<sub>2</sub> complexes have been found for cobalt and iron clusters of certain size.<sup>13</sup> It is possible that such barriers lead to a stabilization of a precursor state to dissociation in which the hydrogen is molecularly coordinated. However, such a state has never been directly observed experimentally.

To probe how hydrogen is bound in Ni<sub>4</sub>H<sub>2</sub><sup>+</sup>, Ni<sub>5</sub>H<sub>2</sub><sup>+</sup>, and Ni<sub>6</sub>H<sub>2</sub><sup>+</sup>, the vibrational spectra of these complexes were recorded under conditions such that only complexes with a single H<sub>2</sub> molecule were present in the molecular beam. Because Ni<sub>4</sub><sup>+</sup> is much less reactive than Ni<sub>5</sub><sup>+</sup> and Ni<sub>6</sub><sup>+</sup>, different conditions had to be used to measure the vibrational spectra of these three complexes. The experimental vibrational spectra of Ni<sub>n</sub>H<sub>2</sub><sup>+</sup>/Ni<sub>n</sub>D<sub>2</sub><sup>+</sup> ( $n = 4-6$ ) complexes are shown in black in Fig. 2. For the complexes with 5 and 6 Ni atoms,



**Fig. 2** Experimental (black) and simulated (red) spectra of Ni<sub>4</sub>H<sub>2</sub><sup>+</sup>, Ni<sub>5</sub>H<sub>2</sub><sup>+</sup> and Ni<sub>6</sub>H<sub>2</sub><sup>+</sup> (bottom to top). The corresponding geometries are shown next to the spectra. The simulated spectrum of Ni<sub>4</sub>H<sub>2</sub><sup>+</sup> is a linear combination with a ratio of 4 : 1 of the spectra of the isomer with molecular H (green dashed line) and dissociated H (blue dotted line) respectively. The experimental spectra are overlaid with a three-point running average to guide the eye.

intense absorption bands are observed in the 1000–1500 cm<sup>-1</sup> range, implying that the H is predominantly dissociatively bound in bridging or face sites.<sup>9</sup> For the Ni<sub>4</sub>D<sub>2</sub><sup>+</sup> complex, a band located at 2460 cm<sup>-1</sup> is observed, proving that there is at least one isomer present in which the D<sub>2</sub> molecule is molecularly bound. The frequency of the D–D stretch band is shifted considerably to lower frequency compared to the frequency of free D<sub>2</sub> (2941 cm<sup>-1</sup>). This implies that the molecularly bound D<sub>2</sub> molecules must be chemisorbed since physisorbed species only show small frequency shifts.<sup>14</sup> A strong absorption band at 680 cm<sup>-1</sup> is observed in the spectrum of Ni<sub>4</sub>H<sub>2</sub><sup>+</sup> but not in the spectra of Ni<sub>5</sub>H<sub>2</sub><sup>+</sup> and Ni<sub>6</sub>H<sub>2</sub><sup>+</sup>, which again points to a different binding of the hydrogen in Ni<sub>4</sub>H<sub>2</sub><sup>+</sup> compared to Ni<sub>5</sub>H<sub>2</sub><sup>+</sup> and Ni<sub>6</sub>H<sub>2</sub><sup>+</sup>. Such bands have been assigned to the Ni–(H<sub>2</sub>) stretch vibration,  $\nu(\text{Ni}-(\text{H}_2))$ .<sup>9</sup> Comparison of the IR-MPD spectrum with simulated spectra supports this assignment. The molecular adsorption of H<sub>2</sub> on Ni<sub>4</sub><sup>+</sup> is remarkable as sites for dissociatively bound H atoms are available and as the dissociative chemisorption of H<sub>2</sub> on nickel surfaces does not proceed *via* a molecular precursor state.

To obtain information on adsorption geometries and bond energies, DFT calculations were performed. The spin and symmetry unrestricted calculations employed the BP86 exchange correlation functional and a TZVPP basis set. Vibrational frequencies and IR intensities were calculated within the harmonic approximation. It has been shown that this approach gives good agreement with experiment.<sup>9,10</sup> Initial complex geometries were generated based on bare metal structures proposed in the literature. For each geometric isomer, calculations were performed for several different spin states. It is known that adsorption of H<sub>2</sub> decreases the total magnetic moment of Ni clusters.<sup>8</sup> Species with molecular or dissociatively bound H are found to be (local) energetic minima. Upon substitution of H by D, all modes, except the

Ni–Ni modes, scale down in frequency by a factor close to  $\sqrt{2}$  ( $\pm 1.2\%$ ). The energy differences between isomers are very small, typically  $\Delta E < 0.2$  eV, which is within the expected accuracy of the calculations. Hence, a ground state geometry cannot be assigned based on energetic considerations alone. Simulated vibrational spectra that provide reasonable agreement with the experimental spectra are shown in Fig. 2 (red) together with the corresponding optimized cluster geometries. Note that the actual structures can be different from the ones shown in Fig. 2. For  $\text{Ni}_4\text{H}_2^+$ , two isomers are required to account for all the absorption features observed in the experimental spectrum (see below). Relative energies, geometries, and vibrational spectra of other isomers can be found in the supplementary information.<sup>†</sup> In agreement with experiment, the hydrogen atoms are dissociatively bound in the isomers of  $\text{Ni}_5\text{H}_2^+$  and  $\text{Ni}_6\text{H}_2^+$  whose vibrational spectra are in best agreement with the experimental spectra. Complexes with molecularly bound  $\text{H}_2$  are at least 0.4 eV higher in energy. In contrast, for  $\text{Ni}_4\text{H}_2^+$ , the lowest energy isomer identified in the calculations, is the complex with molecularly bound  $\text{H}_2$ . The binding energy of the  $\text{H}_2$  molecule is calculated to be 0.5 eV. The calculated frequency of  $\nu(\text{D}–\text{D})$  is too low compared to experiment, while the calculated frequency of  $\nu(\text{Ni}–(\text{H}_2))$  is too high. Both of these observations imply that the calculations overestimate the Ni– $\text{H}_2$  bond strength.<sup>9</sup> In the experimental spectrum of  $\text{Ni}_4\text{H}_2^+$  there is a weak absorption band at  $\sim 1090\text{ cm}^{-1}$ , for which the complex with molecular hydrogen cannot account. It is possible that this band is due to the presence of a second, less abundant isomer in which the hydrogen is dissociatively bound. Indeed the calculations show that there are at least two isomers that have an absorption band around  $1090\text{ cm}^{-1}$  and which are nearly iso-energetic ( $\Delta E = 0.1$  eV), with the complex containing molecularly bound  $\text{H}_2$ . Hence, it is likely that two isomers of  $\text{Ni}_4\text{H}_2^+$ , one with molecularly bound and one with dissociatively bound hydrogen, coexist in the molecular beam. The structures of the complex with molecularly bound hydrogen and of a nearly iso-energetic isomer with dissociatively bound hydrogen are shown in Fig. 2, together with a simulated vibrational spectrum that is a linear combination with a 4 : 1 ratio (isomer with molecular H *versus* isomer with dissociated H) of the spectra of the two individual isomers.

In conclusion, we have demonstrated that a  $\text{H}_2$  molecule can bind molecularly on  $\text{Ni}_4^+$  but that it binds exclusively dissociatively on  $\text{Ni}_5^+$  and  $\text{Ni}_6^+$ . Furthermore, the adsorption behavior correlates with the relative reactivity of the metal

clusters toward  $\text{H}_2$ . This correlation implies that the dissociative chemisorption of  $\text{H}_2$  on  $\text{Ni}_4^+$  is an indirect process; for other small nickel clusters low barriers might exist as well. In that case, the rate determining step is the conversion of the molecular precursor state to the final state where the hydrogen is dissociatively bound. The  $\text{Ni}_4\text{H}_2^+$  isomer with molecular bound  $\text{H}_2$  could be considered as a model for a precursor state to dissociation.

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